COMPUTER SIMULATION STUDIES OF STRUCTURAL RELAXATION IN SUPERCOOLED LIQUIDS SiO\textsubscript{2} AND BeF\textsubscript{2}

F. G. Paladi *, V. J. Gamurari and M. Oguni #

Department of Theoretical Physics, State University of Moldova, A.Mateevici str.60, Chisinau MD-2009, Moldova
#Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo 152-8551, Japan

Molecular dynamics computer simulations of silica and beryllium fluoride by using Morse potential at constant pressure have been performed. We have found that at high temperatures the relaxation times show non-Arrhenius temperature dependence, whereas at low temperatures this dependence is compatible with an Arrhenius law. Our results are in very good agreement with the experimental values for lower temperatures. When liquid is cooled rapidly, the relaxation phenomena of the thermodynamic quantities as well as of the number of bonding atoms in BeF\textsubscript{2} are observed. These quantities are equilibrated in 20 ps, but the time for a significant rearrangement of atoms, i.e. higher atomic motion, is less than 1 ps. A good correlation between micro- and macroscopic parameters used in present simulations has also been suggested.

1. INTRODUCTION

Computer simulation is playing a growing role in academic and industrial research. In areas from physics, chemistry and material science to pharmacy and molecular biology, computer simulation is a part of daily practice. Thus the use of computer simulation is now a very important tool for determining a wide range of properties of many systems, for understanding their structures and dynamics and it is, therefore, a very useful extension of experimental and analytical investigations of many compounds. Processes such as melting, adsorption, formation of clusters and molecular complexes can be analyzed by computer simulation. Such studies may lead not only to improved understanding and insight, but also to practical results such as materials with properties optimized for particular applications. Using the molecular dynamics (MD) computer simulation method the behavior of a variety of molecular systems can be studied. These include liquids, solutions, electrolytes as well as liquid crystals, crystals etc. [1-3].

In this work, MD simulations of the dynamics of silica and beryllium fluoride by using Morse potential at constant pressure [4, 5] have been performed. The first works in this field were done to calculate the frequency of the symmetric vibrational motion between Be\textsuperscript{2+} and F ions in molten BeF\textsubscript{2} at 973 K and to study the structures and dynamic properties of molten NaBeF\textsubscript{2} and Na\textsubscript{2}BeF\textsubscript{4} [6, 7]. The constant pressure model allows us to compare our results with experimental data [8-12]. The conditions of constant volume put some restrictions on the relaxation processes the simulated system may undergo. Constant volume simulations will constrain the system to explore a limited region in amorphous phase space yielding configurations outside the neighborhood of the natural free-energy minimum as some fluctuations may not be allowed. In the studies of phase transitions and glass formations in which volume fluctuations are critical, isobaric ($P=\text{const}$) MD simulations are to be preferred over constant volume MD [5]. The last few years, the dynamics of non-crystalline silica at constant volume was studied by using the microscopic model proposed by van Beest and the static properties as well as the temperature dependence of the diffusion constants were reported [13-15].

2. MODEL AND DETAILS OF THE SIMULATION

Schematic representations of silica and beryllium fluoride are presented in Figure 1. Fig.1 (a) shows that the silicon atoms are surrounded by four oxygen atoms, and the tetrahedra are surrounded

* Author to whom correspondence should be addressed.
Phone: +373-2-577584 Fax: +373-2-240655 E-mail: fpaladi@usm.md
by four other tetrahedra, each of which has a silicon atom in its center. We can also see that six oxygen atoms are the ones that sit in the corners of the two tetrahedra which are connected by the first oxygen atom [15]. Beryllium fluoride has an infinite three-dimensional structure because beryllium, like silicon atoms, is also 4-coordinated (Fig.1(b)) [16]. The properties characteristic for molten BeF$_2$

![Fig.1. Schematic representations of two corner-sharing tetrahedra of silica (a), and of crystal structure of beryllium fluoride (b). $T_g$ and $T_m$ are their glass transition and melting temperatures, respectively.](image)

could be attributable mainly to the fact that owing to the small ionic radii of the both ions the pair potential is much deeper around their mean separation than that between alkali and halide ions [6, 17]. Beryllium fluoride derives its main theoretical importance from its structural similarity to silica because of the similarity in cation/anion radius ratio. Therefore, fluoride melts containing BeF$_2$ serve as low-temperature research analogs for oxide melts containing SiO$_2$ [18].

One of the most important quantities to describe the dynamics of the systems is relaxation time $\tau$, which can be computed from the diffusion constant $D(t)$:

$$\tau = \frac{t_0 d^2}{D(t)},$$

where $t_0 = 10$, $d = 3.5 \text{ Å}$.

On the other hand, the diffusion constant in computer simulations is obtained from the mean square displacement $\langle r^2(t) \rangle$ of a tagged particle:

$$D(t) = \frac{\langle r^2(t) \rangle}{6t},$$

where

$$\langle r^2(t) \rangle = \left\langle [r(t) - r(0)]^2 \right\rangle.$$

In general, provided that a potential barrier $\tilde{A}$ for any molecular rearrangement is independent of temperature $T$, the relaxation time $\tilde{\tau}$ should obey the Arrhenius equation:

$$\tau(T) = \tau_0 \exp \left( \frac{-\tilde{A}}{RT} \right),$$

where $R = 8.31441 \text{ J/(K mol)}$ and $\tau_0$ is interpreted to be related with the frequency of trial for the activation unit to surmount the barrier, and it is in the range of $10^{-13}$ to $10^{-16} \text{ s}$ [19]. This is reasonable in view of the frequency of molecular vibration generally observed. The relaxation times for most supercooled liquids, on the other hand, show a non-Arrhenius behavior: they increase acceleringly with decreasing temperature. The temperature dependence for this so-called $\alpha$-relaxation process is expressed by an empirical equation, namely Vogel-Tammann-Fulcher (VTF) equation [20-22]:

![Fig.1. Schematic representations of two corner-sharing tetrahedra of silica (a), and of crystal structure of beryllium fluoride (b). $T_g$ and $T_m$ are their glass transition and melting temperatures, respectively.](image)
\[ \tau(T) = \tau_0 \exp \left( \frac{A}{T - T_0} \right), \]  

(5)

where \( \tau_0 \), \( A \) and \( T_0 \) are constants. \( T_0 \) is the temperature at which the relaxation time would diverge to infinity. The parameters have different values according to the regions of fitting [23-25]. If the potential barrier \( \Delta \hat{V} \) is independent of temperature, the relaxation time \( \tau \) should obey the Arrhenius equation (4). The non-Arrhenius properties are interpreted as due to increase in the potential barrier along with the decrease in temperature [19].

The model that we used is given by the Morse potential and is of the form [4]:

\[ u_{ij}(r_{ij}) = \frac{Z_i Z_j e^2}{r_{ij}} + f_0 (b_i + b_j) \exp \left[ \frac{(a_i + a_j - r_{ij})}{(b_i + b_j)} \right] + f_0 D_{ij} \left[ \exp \left[ -2\beta_{ij}(r_{ij} - r_{ij}^*) \right] - 2 \exp \left[ -\beta_{ij}(r_{ij} - r_{ij}^*) \right] \right], \]

(6)

where the parameters of O and Si, and those of Be and F are shown in Table 1, \( r_{ij} \) expresses the distance between the ions \( i \) and \( j \), and \( f_0 \) is an arbitrary constant taken to be \( 6.948 \times 10^{-11} \) N, \( Z \) is the ionic charge, \( e = 1.6021892(45) \times 10^{-19} \) C is the unit charge, and \( a \) and \( b \) are the values related to the radius and the compressibility of each ion, respectively.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Z</th>
<th>a / Å</th>
<th>b / Å</th>
<th>Ion pair</th>
<th>D / Å</th>
<th>( \hat{a} )</th>
<th>( r^* / ) Å</th>
</tr>
</thead>
<tbody>
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<td>1.926</td>
<td>0.160</td>
<td>Si-O</td>
<td>74.0</td>
<td>2.0</td>
<td>1.51</td>
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<tr>
<td>Si</td>
<td>2.4</td>
<td>0.945</td>
<td>0.090</td>
<td>Be-F</td>
<td>64.0</td>
<td>2.0</td>
<td>1.39</td>
</tr>
<tr>
<td>F</td>
<td>-0.7</td>
<td>1.890</td>
<td>0.160</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>1.4</td>
<td>0.670</td>
<td>0.090</td>
<td></td>
<td></td>
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</tbody>
</table>

The parameters were determined by trial and error procedures using MD simulations of various oxide crystal structures [4]. The criteria of the determinations were reproducibility of the crystal structures and the calculated pressure in constant cell MDs. Most of the structures were reproduced within mean square displacements of 0.02 Å from the experimentally determined atomic positions and under normal pressure. Thus we conclude that this model gives a realistic description.

The MD calculations started with placing \( N=3000 \) particles (\( N(O)=N(F)=2000 \) and \( N(Si)=N(Be)=1000 \)) inside a basic cell and giving them appropriate initial velocities. The number of particles is large enough to avoid a finite size effect in the dynamics. The equations of motion were integrated with the velocity form of the Verlet algorithm [26] with time step of the integration of \( t=2 \) fs. The longest runs were 1.4 ns at the lowest temperatures of 2900 K and 3100 K which took about 490 h of CPU time for SiO\(_2\) system, and 0.6 ns at the lowest temperatures of 1500 K, 1600 K and 1700 K which took about 210 h of CPU time for BeF\(_2\) system. The Ewald method was applied for the calculations of electrostatic potential and force. The temperature decrement was -0.1 K per one step for all runs. The pressure controlled MD calculations were carried out at 0.0001 GPa. The size of the cubic box \( L_{box}=35.4 \) Å. In order to minimize surface effects periodic boundary conditions were held through the calculations. The masses of the Si and O atoms are 28.086 u and 15.9994 u, and those of Be and F atoms are 10.811 u and 18.998 u, respectively (\( u=1.6605655(86) \times 10^{-27} \) kg).

The starting state was equilibrated at 6500 K for SiO\(_2\) and at 3500 K for BeF\(_2\) by holding the temperature for the calculation of the first 100,000 steps (1 time step corresponds to 2 fs). After the steady state of the internal energy and molar volume was achieved, the temperature was reduced to 6000 K for silica and 3000 K for beryllium fluoride for the next 100,000 steps, and so on. The next investigated temperatures were 5500 K, 5000 K and 4500 K for 100,000 steps, 4000 K for 200,000 steps, 3700 K and 3500 K for 300,000 steps, 3300 K for 400,000 steps, 3100 K and, finally, 2900 K for the last 700,000 steps for silica system, and 2700 K, 2500 K and 2300 K for 100,000 steps, 2100 K and 1900 K for 200,000 steps, 1700 K, 1600 K and, finally, 1500 K for the last 300,000 steps for beryllium fluoride system. Thus the lowest temperatures at which the studied structures could be
equilibrated within the time spans of our simulations were 2900 K for silica and 1500 K for beryllium fluoride.

3. MD SIMULATION RESULTS AND DISCUSSION

3.1. Relaxation-time behavior under equilibrium

Arrhenius plots of the relaxation times for each atom in silica and beryllium fluoride were computed and the results are shown in Figure 2.

We obtained that at high and intermediate temperatures the relaxation times clearly show a deviation from the Arrhenius behavior. However, at the lowest investigated temperatures, our data are compatible with Arrhenius temperature dependence. The experimental data [10-12] are also plotted on these figures by using the Stokes-Einstein relation between viscosity and relaxation time:

$$\tau = \frac{\eta}{G_\infty}, \quad (7)$$

where $G_\infty$ is the high-frequency limit of shear-modulus. If the temperature dependence of $G_\infty$ is ignored (because it is very small), $G_\infty$ is recognized to have the value of $10^9$ Pa in the order of magnitude [27]. These experimental data for lower temperatures fit very well theoretical results. Thus from our simulations we can remark that, with increasing temperature, real silica and beryllium fluoride will make a transition from being strong glassformers, which show an Arrhenius temperature dependence of the transport coefficients, to fragile glass formers.

In order to obtain Arrhenius plots by using Eqs.(1) and (2), we need first to know the slope of the time dependence of mean square displacement $\langle r^2(t) \rangle$ of tagged atoms. These data for $T=1700$ K and $2500$ K in the case of BeF$_2$ system are shown in Figures 3(a) and 3(b), respectively. At the lowest temperatures the dependence shows small deviations from a straight line (Fig.3(a)), but this behavior will not decrease the precision of our final results, because the running time $t=600$ ps (300,000 steps) is long enough to equilibrate BeF$_2$ system at the lowest temperatures and, by the end of computation, diffusivity shows a constant value (Fig.3(c)). The effect of fast increase of mean square displacement during 10-20 ps at first stage of computer simulations for each temperature is caused by a high non-equilibrium state of the system and these values have not been taken into account in processing data under equilibrium.

These results obtained under equilibrium are used as starting data in next section to study properties of beryllium fluoride in case of irreversible relaxation under non-equilibrium.
3.2. Properties of irreversible relaxation under non-equilibrium

When liquid is cooled rapidly, the molecules are frozen in some arrangement, and the relaxation phenomena of the thermodynamic quantities such as internal energy $U$ and volume $V_m$ were observed (Fig.4). The temperature decrement of 0.1 K per one step for runs wasn’t used in these computer simulations in order to obtain a sudden temperature change effect. The observed thermodynamic quantities are considered to be equilibrated in 20 ps. Since liquid is expected to have some microscopically heterogeneous structure due to the presence of clusters, there should exist a distribution in the energetic circumstances of molecules and thus in the response functions for the elementary rearrangement units.

The results presented in Figure 5 show the distribution of Be (Fig.5(a)) and F (Fig.5(b)) atoms, $N_{\text{atom}}/ds$, as a function of their total trajectory length $s$ for 15 running steps started at different time moments (0.1, 1, 5, 10, 20, 30, 40, 100 and 597 ps), after temperature was suddenly changed from 2500 K to 1700 K. In order to obtain $N_{\text{atom}}/ds$, the sum of the trajectory length at each step and for each particle ($N=3000$) was taken for all intervals of trajectory during 15 running steps started at different time moments which are shown above. We classified total trajectory length for all atoms into 40 groups with step $(s_{\text{max}} - s_{\text{min}})/40$, where $s_{\text{max}}$ and $s_{\text{min}}$ are:

Fig.4. Relaxation of internal energy and volume of BeF$_2$ system when temperature was suddenly changed from 2500 K to 1700 K.

Fig.5. Distribution of Be (a) and F (b) atoms, $N_{\text{atom}}/ds$, as a function of their total trajectory length $s$ for 15 running steps started at different time moments (0.1, 1, 5, 10, 20, 30, 40, 100 and 597 ps), after temperature was suddenly changed from 2500 K to 1700 K.
$s_{\text{max}}$ are the maximal and minimal values of $s$, respectively, to obtain the distribution $N_{\text{atom}}$ as a function of total trajectory length $s$, and then we divided the result of each group to the trajectory length corresponding to that group. $N_{\text{atom}}/ds$ obtained in this way gives information about a new distribution with constant curve area due to constant number of Be and F atoms, and describes in detail the dynamics of the system, because we can take into account each movement of the atom even if it comes back to the previous position at next step. We can conclude that the time for a significant rearrangement of atoms is less than 1 ps and during this period a longer trajectory length $s$ (i.e. a higher chaotic motion) than square root of mean squared displacement, $\sqrt{\left\langle r^2(t)\right\rangle}$, is expected (the ratio is about 20). This can be the reason for the fact that the period of significant changes in the rearrangement of atoms is less than that for the relaxation of the thermodynamic quantities.

Figure 6 shows time dependences of the number of bonds, $N_{\text{bond}}(t/\text{ps})$, for BeF$_2$ system when temperature was suddenly changed from 2500 K to 1000 K, 2500 K to 1700 K, and 2500 K to 2100 K. In order to study these time dependences, we needed to know first the distance between Be and F atoms for which Be-F pairs are connected by bonds. For this purpose, radial distribution functions of F atoms surrounding Be atoms at $T=1000$, 1700 and 2100 K were computed, and we obtained that it is about 2.4 Å. Therefore, Be-F pairs separated by less than 2.4 Å are considered to be connected by bonds. This distance is in good agreement with the result derived from X-ray diffraction [28], and has given a realistic illustration of the network structure of BeF$_2$ [29]. We can see in Fig. 6 that cooperative rearrangement motion involves breaking/forming of bonds in BeF$_2$ mainly during the first 20 ps of computer simulations, and the fluctuations of the number of bonds decrease for higher magnitude of temperature jump (or lower final temperature). These results are in good agreement with those of the relaxations of the thermodynamic quantities described above, and show a good correlation between micro- and macroscopic parameters.

![Fig. 5. Distribution of Be (a) and F (b) atoms as a function of trajectory length. Temperature was suddenly changed from 2500 K to 1700 K.](image)

![Fig. 6. Time dependence of the number of bonds for BeF$_2$. Temperature was suddenly changed from 2500 K to 1000 K, 2500 K to 1700 K, and 2500 K to 2100 K, respectively. Be-F pairs separated by less than 2.4 Å were connected by bonds.](image)
4. CONCLUSION

The analogy between SiO$_2$ and BeF$_2$ in MD computer simulations appears to be an excellent one in many respects and predicts, in part, the similarities between these two systems in crystal structure and temperature dependence of their viscosities. A good correlation between micro- and macroscopic parameters was confirmed by the present research. This leads to a reasonable conclusion that the investigations of the relaxation phenomenon in computer simulation promise to yield valid information about the fluctuations and irreversible relaxation in the structures of liquids and glasses.

We can study the structure in full microscopic detail due to the fact that for most atomic systems dynamical phenomena occur on a time scale that is accessible to such simulations, i.e. happen between $10^{-12}$ and $10^{-7}$ s. More complex systems can also be investigated by using the same tool, improving the theoretical models and verifying their validity by comparing with experimental data. Moreover, most of the computer simulations were done so far for liquids for which the local structure is similar to that of a close-packed hard-sphere system, but the dynamics of systems in which the particles form an open network structure, such as SiO$_2$ and BeF$_2$, have hardly been studied, although there are many experimental results in this field [30, 31]. The use of a new method for identifying clusters based on maximization of the entropy [32] is also applicable. It reflects more closely the thermodynamic process of merging and splitting involved in the real systems and employs minimal constraints on the cluster assignments as well as any final structures are only due to the nature of the interaction between the molecules. This would be very significant in making a real picture for the relaxation phenomenon and promises to develop a generally applicable to different branches of cluster analysis algorithm because of a general probability function.

REFERENCES